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Internal Stresses in Bulk Metallic Glass Matrix Composites

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ABSTRACT
Composites consisting of a bulk metallic glass (BMG) matrix and metallic fibers or particulates have been shown to exhibit superior mechanical properties as compared to monolithic BMGs. To understand the role of reinforcements in this improvement, it is necessary to investigate the state of internal stresses in these composites. These stresses arise from the thermal expansion mismatch between the reinforcement and the matrix, as well as the elastic and plastic incompatibilities between the two phases. Neutron diffraction and synchrotron X-ray diffraction were used to measure these mismatch-induced stresses in BMG-matrix composites with various reinforcements: continuous W fibers, W or Ta particles, and dendritic, *in-situ* formed precipitates. The results are compared to numerical and analytical predictions of internal stresses.

INTRODUCTION
Bulk metallic glasses (BMGs) have recently attracted widespread interest due to the development of new alloys that yield a glassy structure even with "conventional" metal processing such as casting [1]. The unique properties of BMGs potentially place them among significant engineering materials: very high strength (1.9 GPa) and fracture toughness (40-55 $MPa.m^{1/2}$), a near theoretical specific strength, excellent wear and corrosion resistance, and a high elastic strain limit of up to 2% [2,3]. A major drawback of BMGs is that they fail catastrophically when unconstrained (e.g., in uniaxial tension) by forming localized shear bands. To avoid this and to obtain more damage tolerant BMGs, they are reinforced with fibers or particulates [4,5,6]. These studies demonstrated that the composite approach could be quite beneficial. The reinforcements seem to interact with the shear bands and sometimes act as obstacles against their propagation. Despite these significant improvements, there are a number of unresolved fundamental issues about how exactly the reinforcements interact with the shear bands. In addition, the 'best' reinforcement and its morphology are yet to be identified.

A critical issue in the BMG-matrix composites is the presence of internal stresses. These stresses are either due to the coefficient of thermal expansion (CTE) mismatch between the matrix and the reinforcements or they arise from the elastic and plastic incompatibilities between them during mechanical loading. Since these stresses are predicted to reach several hundred MPa (4), they are expected to significantly influence the mechanical behavior of the composites. As part of a systematic study on the interactions between the matrix and reinforcements in BMG composites, this article presents preliminary results from diffraction experiments on three types of composites with the following crystalline reinforcements: (i) continuous W fibers; (ii) W or Ta particles; and (iii) dendritic precipitates formed *in situ* during processing.

EXPERIMENTAL PROCEDURE

The W-fiber/BMG composites consisted of unidirectional W fibers of about 250 μm in diameter and a BMG alloy (Vitreloy 1™: $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$) matrix. Composites with four different fiber volume fractions (20, 40, 60 and 80%) were studied in terms of their thermal residual stresses using neutron diffraction (ND) [7]. Specimens were cylinders of about 50.0 mm in length and 7.75 mm in diameter (aspect ratio of 6.5). The processing technique was melt infiltration casting and is described elsewhere in detail [8]. A variation of this method was also used in making composites with 5 or 10 vol.% W and Ta particles [6]. The matrix in these composites was Vitreloy 106 ($Zr_{57}Nb_5Cu_{15.4}Ni_{12.6}Al_{10}$). The particulate composites were subjected to a tensile load while being investigated with synchrotron X-rays [9]. The last type of composite studied consisted of dendritic ductile phase precipitates in a BMG matrix. These particles were made of a BCC alloy (called the "β-phase") with mostly Zr, Ti and Nb in it and precipitated *in situ* during processing (see ref. [10] for details). The latter composite was also investigated with ND, but under compressive uniaxial loading.

The ND experiments were conducted on the Neutron Powder Diffractometer at the Los Alamos Neutron Science Center (LANSCE). LANSCE employs spallation neutrons and the time-of-flight (TOF) technique, which means that entire diffraction patterns (for a certain range of *d*-spacings) are measured simultaneously by, in this case, two detector banks at scattering angles of ±90°. In this arrangement, the $2\theta = -90°$ detector measures the longitudinal lattice strain while the $2\theta = +90°$ detector determines the transverse strain. The diffraction data were analyzed using the Rietveld method [11,12]. The following parameters were refined (in order): scale factor; background, lattice parameter, orientation distribution function for texture, absorption, extinction, and isotropic atomic displacements (see ref. [7] for details).

The XRD studies were performed at the Advanced Photon Source (APS), Argonne National Laboratory. A monochromatic, parallel X-ray beam with 65 keV energy penetrated the sample in a direction perpendicular to the loading axis. Transmitted low-index diffraction rings were recorded with a two-dimensional CCD camera and volume-averaged reinforcement strains were determined from the slight ellipsicity of these diffraction rings, as described in ref. [13].

RESULTS AND DISCUSSION

W-fiber/BMG-matrix Composites

The main source of internal stress investigated in these composites is the CTE mismatch between the fibers and the matrix. The fibers have a room-temperature CTE value of about 4.6×10^{-6} K^{-1} while the matrix has a widely varying CTE of about 9.0×10^{-6} to 15×10^{-6} K^{-1} [7]. In this case, the smaller CTE of W is predicted to lead to less contraction in the fibers compared to that in the matrix during cooldown from the processing temperature. As a result, the fibers will be placed in axial compression and transverse tension (on average).

Because of the amorphous structure of the matrix, the ND measurements provide information only about the residual strains in the W fibers. To estimate the stress and strain state in the BMG matrix, a finite element (FE) model was developed using a commercial software (ABAQUS™). In this model, the fiber stacking was hexagonal and a two-dimensional plane strain state was assumed. The interface between the fibers and the matrix was assumed to be intact at all times, an assumption supported by other studies [5]. Both W and BMG are elastically isotropic materials. In the FE model, they were also considered to be elastic at all temperatures of interest. Additional details about the FE calculations are presented in ref. [7].

The measured average residual strains in W (Fig. 1) follow an expected trend. The Rietveld refinement revealed a very strong [110] texture along the axis of the W fibers, most probably from the drawing process used to fabricate them. The refinement residuals were quite low (~6%) indicating a good fit to data. To quantify the systematic experimental errors, especially the displacement error in the diffractometer, the 80% W composite was subjected to five independent measurements. The results suggest that the uncertainty in the W lattice constant values is within ±100 με. This number is used for the error bars shown in Fig. 1.

The FE calculations were performed by treating the effective temperature range during cooling, ΔT, as a free variable. The best fit to the neutron data was found to be ΔT=335 K. Such a value indicates that thermal residual stress buildup started around 628 K which is within the glass transition range of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.}Be_{22.5}$ [14]. It is interesting to note that a simple, elastic FE model can predict the residual stress development in this system. This means that, for the cooling rates used experimentally, the BMG matrix can be effectively regarded as an elastic material right below its glass transition. To check the validity of this claim, some stress relaxation time calculations were performed using the viscosity data for this alloy [7]. The results show a very rapid change in relaxation time with temperature around the glass transition region for this BMG alloy. They also indicate reasonable time scales that could be valid during the processing of the W/BMG composites. Therefore, the effective "freezing" temperature predicted by the FE calculations (628 K) is a reasonable value below which the BMG matrix can be regarded as an elastic solid in practice.

Once a suitable FE model was identified, the residual strains and stresses were determined in the matrix and the stresses were calculated in the fibers. These stresses are significant in both phases [7] and are expected to affect their *in-situ* mechanical behavior during the loading of the composites. Another important result of the FE calculations is illustrated in Fig. 2. Here the distribution of the von Mises stresses, $\sigma_{vM} = \{(\sigma_{11} - \sigma_{22})^2 + (\sigma_{11} - \sigma_{33})^2 + (\sigma_{33} - \sigma_{22})^2\}^{1/2}/\sqrt{2}$, in the 80% W/BMG composite are shown. It is seen that while ND studies determine only the average strains in the W fibers, the FE calculations predict severe stress concentrations (up to

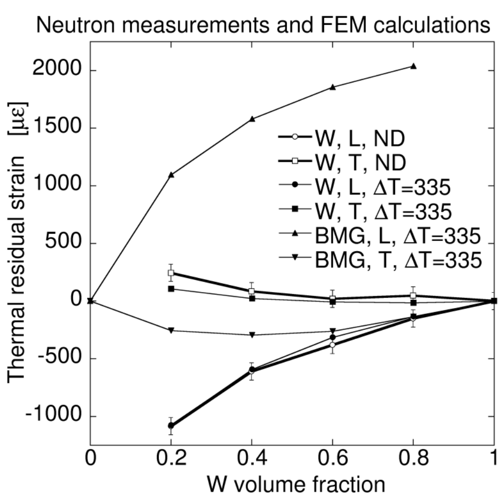

Figure 1. Thermal residual strains in W-fiber/BMG composites. A comparison of FE calculations with ND data from W fibers is shown. The strains in the BMG are FE predictions. ΔT indicates the effective cooling range during which these strains are built. (L: longitudinal, T: transverse)

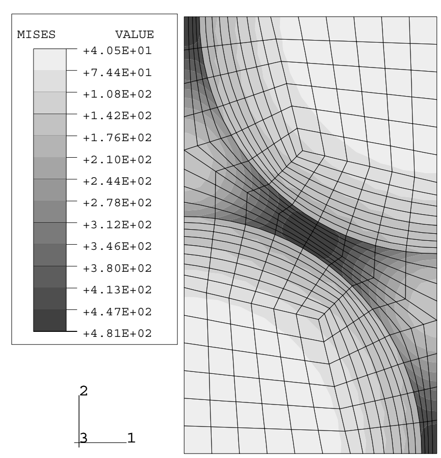

Figure 2. Finite element prediction of von Mises stresses in the 80% W/BMG composite. The maximum value of these stresses is over 480 MPa between fibers (dark gray areas).

about 480 MPa) in the matrix regions where fibers are closest to each other. These are the areas where shear bands will most likely be initiated.

BMG Composites with W or Ta Particles

These composites were investigated to determine the *in-situ* load transfer characteristics between matrix and reinforcements. While more extensive results on all composites studied are presented elsewhere [9], here some results for the 5 vol.% W/BMG composite are briefly discussed. Fig. 3 shows the evolution of the internal elastic strains along the loading axis in the W particles. Note that residual elastic strains from cooling are not shown and would shift the points along the x-axis. Fig. 3 shows an initial linear elastic response in W, followed by yielding at about 600 MPa applied stress and plastic deformation up to 1 GPa. Unloading occurs purely elastically, thus resulting in a residual compressive strain of about -1000 $\mu\varepsilon$. Subsequent reloading results in a purely elastic response of the W particles up to 1 GPa, followed by plastic deformation. Qualitatively, these results indicate that: (i) yielding occurs in the W particles at about 600 MPa applied stress upon initial loading and about 1 GPa upon subsequent loading due to strain-hardening; and (ii) bonding between particles and matrix is not degraded after the first mechanical cycle, as the elastic load-transfer during the second loading is unchanged (same slopes). To determine the *in-situ* yield stress of the W, the von Mises stresses were calculated from the experimental strain data (Fig. 4). These stresses can be compared to those calculated by an elastic Eshelby model [9], which predicts the correct slope (i.e., load transfer) in the elastic region. Also, yielding occurs at about 800 MPa von Mises stress in the W particles, a value that is similar to literature data. This suggests that no significant change in the W mechanical properties occurred as a result of processing.

Qualitatively similar behavior was also observed in the other two composites containing 10 vol.% W and 5 vol.% Ta particles. They also showed reinforcement plasticity and compressive residual strains upon unloading. The *in-situ* yield stresses of the W and Ta particles were found to be about 850 and 200 MPa, respectively [9]. Both values are typical for these metals.

As discussed in the previous section, compressive residual stresses are expected in the W and Ta particles due to the CTE mismatch with the matrix. A detailed discussion of the possible effects of the thermal residual stresses will be presented elsewhere [9].

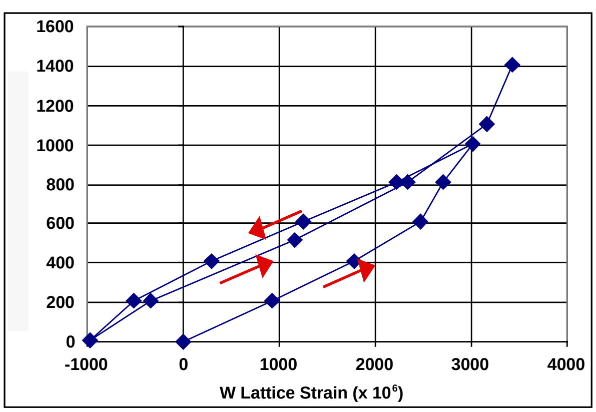

Figure 3. Variation of longitudinal elastic strain in W particles as a function of applied stress in the 5 vol.% W/BMG composite. The specimen was first loaded to 1 GPa, then unloaded and finally loaded again to failure.

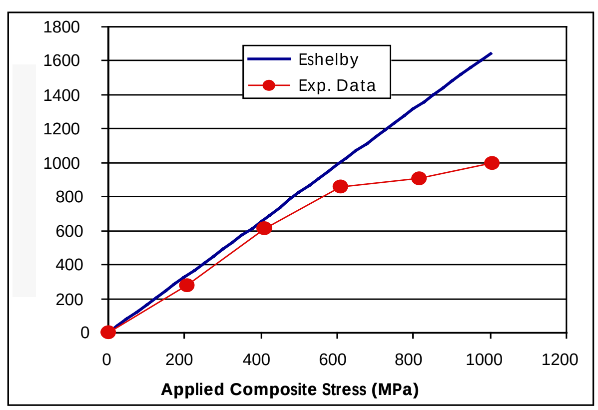

Figure 4. Comparison of von Mises stresses from an elastic Eshelby model to those obtained from the experimental data in the 5 vol.% W/BMG composite. Only the first loading part is shown. The W particles show yielding at about 800 MPa.

"β-Phase" Composites

These composites consist of a BMG matrix with a composition close to that of Vitreloy 1 and a dendritic second phase (the "β-phase") with a BCC structure. The "β-phase" was about 25 vol.% and formed *in situ* during processing; it contains mostly Zr, Ti and Nb [10]. Such processing provides an attractive means to manipulate the microstructure and hence influence the mechanical properties of the composite. The "β-phase" was found to induce significant ductility and toughening in composites [10], however, the exact mechanism that achieves this is unknown at this moment. A systematic study using ND is underway [15] to determine this mechanism and some preliminary results are presented here.

In-situ compression tests were performed during ND experiments on a composite and a reference monolithic "β-phase" alloy. The latter had been prepared under similar conditions used for the composites and had the same chemical composition of the second phase found in these materials. The results are shown in Figs. 5-6. No significant plasticity was detected in either specimen. This is contrary to earlier mechanical tests [10,16] which showed yielding in the "β-phase" at around 550 MPa. The monolithic "β-phase" alloy used in ND studies was tested in compression separately [15] and failed in a brittle manner at 1425 MPa. The lack of plastic deformation in the ND specimens is attributed to oxygen embrittlement. It is hypothesized that more oxygen was dissolved in those samples during processing compared to the earlier ones which yielded at 550 MPa. Chemical analyses on all "β-phase" specimens are underway to determine their exact oxygen concentration and will be reported elsewhere [15].

The ND experiments also failed to show any stress-induced phase transformation in the "β-phase". This had been proposed as another operative mechanism in the composites due to the shear instability in this phase [10]. The presumed excess oxygen in the ND specimens may have influenced this behavior as well. New specimens were investigated recently at LANSCE to clarify this issue; the data analysis is underway.

CONCLUSIONS

Neutron diffraction (ND) and synchrotron X-ray diffraction (XRD) were used to study the bulk, average internal stresses in the crystalline reinforcements of BMG-matrix composites. These stresses arise from the CTE mismatch between the reinforcements and matrix as well as the

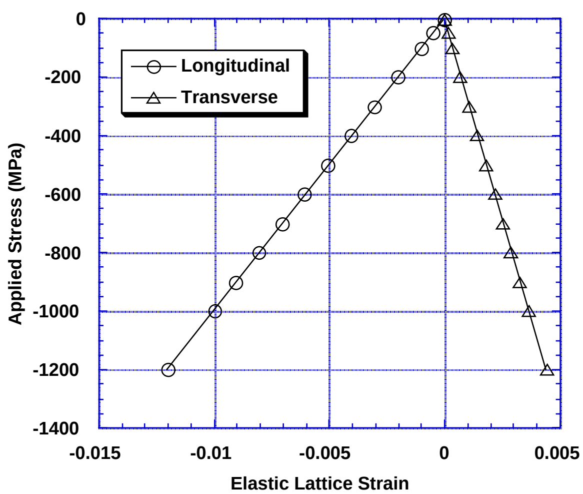

Figure 5. Compressive loading on a monolithic "β-phase" alloy. The strains were measured with ND.

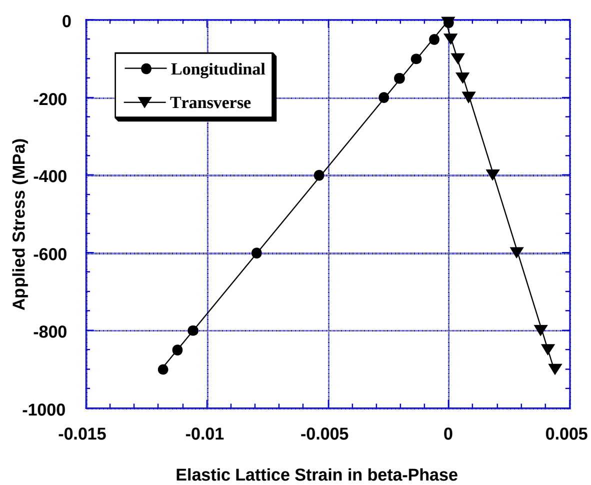

Figure 6. Compressive loading on a "β-phase"/BMG composite. The strains in the "β-phase" were measured with ND.

elastic and plastic incompatibilities between the two under loading. The specific conclusions reached regarding the three types of composites studied are:

W-fiber/BMG-matrix composites: Significant residual thermal strains were measured by ND in the fibers. These could be accurately described with an elastic finite element model which also predicted peak matrix stresses as high as 480 MPa in regions between fibers. The "freezing" temperature below which stress buildup starts during cooling was found to be near the glass transition temperature of the matrix.

W or Ta particulate composites: Tensile loading experiments were performed on these materials. Elastic load transfer between matrix and particles was measured by XRD and found to be in good agreement with Eshelby predictions. Plastic yielding occurred in the particles with *in-situ* yield strengths close to literature data. Upon unloading, residual compressive stresses thus developed. Upon subsequent reloading, the elastic load-transfer was unchanged, indicating that the interface between particles and the matrix was not damaged during the previous mechanical cycle. Particle yielding then occurred at a significantly higher stress, as expected from strain-hardening of the particles.

"β-phase" composites: These *in-situ* composites were studied under compression using ND. Specimens deformed elastically and did not show any stress-induced phase transformations. This is likely due to the excess oxygen present in these materials.

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